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(54) COPOLYMERE TETRAFLUORO ETHYLENE/HEXAFLUORO PROPYLENE AYANT UN HAUTE APTITUDE A L'ETIRAGE AMELIOREE

(54) TETRAFLUOROETHYLENE/HEXAFLUOROPROPYLENE COPOLYMERS WITH HIGHER DRAWABILITY

(57)

²²²The invention relates to a fluorinated ethylene propylene copolymer which is ²processed from the melt by fusion granulation and which consists essentially ²of monomer units of 78 to 95 wt. % tetrafluoroethylene, 5 to 22 wt. % ²hexafluoropropene and not more than 3 mol % fluorinated monomers that can be ²copolymerised with a mixture of tetrafluoroethylene and hexafluoropropene. ²Said copolymer has a molar ratio of weight average to number average of less ²than 2, has less than 80 unstable terminal groups per 1x10⁶ carbon atoms and ²is produced by aqueous emulsion polymerisation. The copolymer is coagulated ²after polymerisation and then agglomerated. The agglomerate is isolated and ²dried to form a free flowing product, partial sintering being prevented. Said ²product is brought into contact with an effective amount of fluorine at a ²temperature between 60 ~C and the preliminary sintering temperature, whereby ²unstable terminal groups are converted into stable terminal groups. The fusion ²granulate is advantageously treated with ammonia or a compound which liberates ²ammonia, in water. The product can be used for coating wires and cables.²



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(57) Abrégé/Abstract:

The invention relates to a fluorinated ethylene propylene copolymer which is processed from the melt by fusion granulation and which consists essentially of monomer units of 78 to 95 wt. % tetrafluoroethylene, 5 to 22 wt. % hexafluoropropene and not more than 3 mol % fluorinated monomers that can be copolymerised with a mixture of tetrafluoroethylene and hexafluoropropene. Said copolymer has a molar ratio of weight average to number average of less than 2, has less than 80 unstable terminal groups per 1×10^6 carbon atoms and is produced by aqueous emulsion polymerisation. The copolymer is coagulated after polymerisation and then agglomerated. The agglomerate is isolated and dried to form a free flowing product, partial sintering being prevented. Said product is brought into contact with an effective amount of fluorine at a temperature between 60 °C and the preliminary sintering temperature, whereby unstable terminal groups are converted into stable terminal groups. The fusion granulate is advantageously treated with ammonia or a compound which liberates ammonia, in water. The product can be used for coating wires and cables.

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Description

Tetrafluoroethylene/Hexafluoropropylene Copolymers with Higher Drawability

5 Field of the Invention

The invention relates to melt-processable tetrafluoroethylene (TFE)/hexafluoropropylene (HFP) copolymer melt pellets having improved processability for wire and cable applications and to a process for using this polymer to coat wire and cable conductors.

10 Background

Melt-processable copolymers with TFE and HFP are best known under the name FEP. As perfluorinated thermoplastics, such copolymers have unique end-use properties like chemical resistance, weathering resistance, low flammability, thermal stability and outstanding electrical properties. Like other thermoplastics, FEP is easily molded to give
15 coated wires, tubes, pipes, foils and films.

Because it has excellent thermal stability and is practically non-flammable, FEP is frequently used in the design of multiple-occupancy rooms and meeting halls, to meet stringent fire protection requirements. FEP is also the natural choice in data transmission
20 cables due to its excellent dielectric properties (EP-A-423 995).

High processing speeds are desired when wires and cables are extrusion coated. However, melt fracture limits these high extrusion rates in the case of many thermoplastics. Melt-fracture results in surface roughness and/or uneven wall thickness. To increase the
25 extrusion speed it is therefore assumed that the molecular weight distribution of the copolymer used should be very broad as disclosed, for example, for the FEPs in US-A-4,552,925.

For substantial broadening of the molecular weight distribution, use is mostly made of a
30 mixture of at least two FEPs with markedly differing molecular weights. The molecular weights are usually characterized by the melt viscosity or the melt flow index (MFI value). The mixtures desired are often produced by polymerizing the components separately and

mixing them in the form of latices, beads or unconsolidated products before melt pelletizing. Thus the manufacture of these mixtures is a cumbersome and costly process.

Other FEP mixtures are disclosed in DE 26 13 642 and DE 26 13 795.

5

These mixtures are claimed to be advantageous therein for suppressing foaming during the FEP stabilization. This process is carried out by treating the resin at high temperatures (up to 400° C), preferably with water vapor. This process removes the thermally unstable end groups, mostly COOH and CONH₂ groups. These end groups may easily be detected by

10

IR spectroscopy.

These mixtures have a very broad molecular weight distribution, and this is generally understood by the skilled worker to give improved extrudability.

15

Removal of thermally unstable end groups is required for the processing of FEP, in particular for wire coatings. The decomposition reaction of the unstable end groups, described in Modern Fluoropolymers, editor John Scheirs, Wiley & Sons, 1997, page 228 leads to bubbles and holes in the final products. Melt pelletizing of unstabilized polymer resins results in corrosion of the equipment used and in metal contamination of the melt pellets produced. However, the stabilization processes of DE 26 13 642 and DE 26 13 795 are very difficult to carry out, since they give rise to problems of corrosion of the equipment used, due to the use of water vapor.

20

25

Metal contaminants are difficult to control and may result in degradation and decomposition of the copolymer at high processing temperatures. This decomposition generally leads to discoloration and degradation, and to a build up of die deposits. Die deposits are accumulations of molecular fractions of the polymer on the surface of the die orifice, and adversely affect the coating process. The phenomenon known as cone fracture can also occur. During the process of coating a wire, the molten polymer is extruded as a tube or sheath and drawn by vacuum onto the wire. Cone fracture is discontinuity or fracture that occurs during this process. Every time this type of cone fracture occurs, the coating process has to be re-initiated and there is a waiting time for the system to reach

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equilibrium again. Thus long operating times are difficult to achieve. Productivity is also reduced.

Furthermore, extrusion temperatures have to be kept as low as possible to inhibit decomposition reactions and the resultant evolution of toxic gases, the rate of which substantially increases as the temperature rises. On the other hand, lower extrusion temperatures result in higher melt viscosities and thus earlier onset of melt fracture. Lowering the intrinsic melt viscosity by lowering the molecular weight results in poorer mechanical properties.

To render the material more thermally stable, therefore, it is necessary not only to eliminate the thermally unstable end groups but also to avoid metal contamination and Mw fractions which are relatively prone to shear degradation and/or to thermal degradation.

Another way to eliminate unstable end groups is postfluorination, for example as disclosed in GB-A-1 210 794, US-A-4 743 658 and EP-B-457 255. This process generally uses elemental fluorine diluted with nitrogen at elevated temperatures up to the melting range of the polymer. When subjected to fluorination the polymer here may be in the form of melt pellets, agglomerates or unconsolidated material. Here, too, excessive metal contamination should be avoided.

EP-B-222 945 discloses the fluorination of hardened agglomerates, there called granules.

The fluorination leads to perfluorinated end groups whereas the humid heat treatment described above cannot mechanistically result in a fully fluorinated polymer resin. It is believed that inserted double bonds are present here in the main chain of the polymer and lead to inherent thermal instability. These bonds may lead to the discoloration seen on long exposure to high temperatures.

Another degradation reaction of FEP is disclosed in US-A-4 626 587. The onset of this reaction is supposed to occur firstly by splitting of the HFP diads in the middle of the chain at temperatures above the melting point. These diads are formed in the free-radical

polymerization reaction by recombination of the corresponding polymer radicals in a termination step. The destruction of the diads under processing conditions leads to halving of the molecular weight of these polymer chains, adversely affecting mechanical properties of the polymer, and to formation of end groups which are more unstable. As
5 US-A-4 626 587 teaches, these diads are destroyed by subjecting the material to very high shear rates at a temperature markedly above the melting point. This process is also very costly.

Another process for reducing the instability of the main chain is disclosed in EP-A-789 038.
10 The process uses relatively large amounts of a chain transfer agent to suppress termination of polymer radicals.

Summary of the Invention

The present invention provides a material which can be used for wire and cable coatings
15 and which can be processed at higher speeds and at higher temperatures, giving longer running times for machinery. The invention furthermore provides a manufacturing process which is more economical and more controllable for consistency of quality. Still further, the invention provides a process for reducing die deposits and the frequency of cone fracture during the extrusion coating of wires or cables.

20

Detailed Description

The polymer according to the invention is a copolymer of TFE and HFP. It has an HFP content in the range from 5 to 22% by weight, preferably from 10 to 18% by weight, a TFE content of from 95 to 78% by weight, preferably from 90 to 82% by weight, and
25 optionally contains up to 3 mol% of a fluorinated monomer copolymerizable with HFP and TFE. The optional comonomer is preferably a perfluoro alkyl vinyl ether as is disclosed in EP-A-789 038 and DE-C-27 10 501. The monomer content may be measured via IR spectroscopy as described in US-A-4 552 925. The polymers of the invention typically have a melting point of from 240 to 275°C, preferably 245 to 265°C.

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The polymer of the invention is essentially free of thermally unstable end groups, these being removed via postfluorination of the agglomerates. "Essentially free of end groups"

means fewer than 80 end groups per million carbon atoms, preferably fewer than 40 end groups and particularly preferably fewer than 30 end groups per million carbon atoms. The material is essentially of high purity with respect to metals, i.e. the total amount of iron, chromium and nickel is less than 200 parts per billion (ppb), preferably less than 100 ppb.

5

The polymer of the invention used to coat wire and cable conductors has a very narrow molecular weight distribution, i.e. a ratio of Mw to Mn of less than 2 (Mw = weight average, Mn = number average molecular weight). This ratio may be as low as 1.5. This is in contrast to FEP grades recommended for wire coating with high extrusion rates, a broad molecular weight distribution being recommended for those grades. The broadness of the molecular weight distribution is measured according by the method of W. H. Tuminello in Polym. Eng. Sci 26, 1339 (1986). For high speed wire extrusion the MFI of the polymer is ≥ 15 . Lower MFIs are useful for other applications, such as foamed coaxial cable. This polymer is preferably essentially free of unstable end groups. It is very particularly preferably the polymer of the invention.

15

A melt pelletized copolymer according to the invention with an MFI value of 24 and 15% of HFP may be produced as described below. This polymer can be extruded with a wire coating extruder at, for example, 390°C (735°F) at a rate of 454 m/min (1500 feet/min) over a machinery running time of 6 hours without discoloration and without producing any substantial amount of die deposit and with less cone fracture than commercial FEP grades. The surprisingly good performance is not fully understood.

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Despite narrow molecular weight distribution, high processing rates can be achieved. As has been discussed above, the art teaches that broad molecular weight distribution is needed to achieve such high processing rates. It has now been discovered that narrow molecular weight distribution is better, thus overcoming a well-established prejudice.

25

Furthermore, no discoloration occurs during processing. This is an indication of the absence of any decomposition reaction. The MFI value of the extruded material is practically unchanged. The amount of IR-detectable end groups does not increase. Both findings indicate that there is no significant chain degradation. This observation indicates

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that the material has no weak linkages in its main chain, for example HFP diads (US-A-4 626 587).

5 The non-occurrence of discoloration, the almost unchanged MFI value and the almost unchanged number of end groups are evidence of the absence of any significant decomposition even at relatively high processing temperatures. It is believed that this results in reduced die deposits and the markedly reduced frequency of cone fracture. Hence, the copolymer according to the invention exhibits surprisingly high thermal stability even under shear. The polymer of the invention can therefore also be used
10 advantageously in other applications.

The evidence of the absence of decomposition reactions is surprising and not fully understood. It is believed that metal contaminants, in particular heavy metals, such as iron, nickel or chromium, may induce a decomposition reaction. Indeed, neutron activation
15 analysis showed that the amount of ions of iron, nickel and chromium in the material used was very low: below 50 ppb. Thus the copolymer according to the invention can be classified as of high purity.

The polymer of the invention may be produced by the process described below.
20

The polymerization may be carried out as free-radical aqueous emulsion polymerization of the prior art (see US-A-2 946 763). Ammonium or potassium peroxodisulfate may be used as initiators. As emulsifiers, use may be made of standard emulsifiers, such as the ammonium salt of perfluorooctanoic acid. Buffers, such as NH_3 , $(\text{NH}_4)_2\text{CO}_3$ or NaHCO_3 ,
25 may be added to the formulation. Typical chain transfer agents, such as H_2 , lower alkanes, methylene fluoride or methylene chloride are used. Chlorine- or bromine-containing chain transfer agents should be avoided. These components may cause marked corrosion during fluorination. The polymerization temperature can range from 40 to 120°C, preferably from 50 to 80°C; the polymerization pressure may range from 8 to 25 bar, preferably from 10 to
30 20 bar. HFP forms as initial charge and is fed into the reactor according to the rules of copolymerization [see, for example, "Modern Fluoropolymers", editor John Scheirs,

Wiley & Sons, 1997, page 241). The preferred polymerization formulation is free from alkali metal salts.

5 Furthermore, it is preferable to carry out the copolymerisation without use of any chain transfer agent, in contrast to EP-A-789 038. Chain transfer agents intrinsically broaden the molecular weight distribution. The polymerization rate/time curve should have the shape as published in "Modern Fluoropolymers", editor Johns Scheirs, Wiley & Sons, 1997, page 226. As stated in that publication, the Mw/Mn ratio can be easily calculated from the rate/time curves in the absence of any chain transfer agent via equation (6), page 230 and
10 assuming that termination occurs solely via recombination. Recombination leads to an Mw/Mn ratio of 1.5 for small conversions. Termination primarily via chain transfer leads to an Mw/Mn ratio of 2.

The free-radical polymerization may also be carried out in a nonaqueous medium, such as
15 R 113, as disclosed in US-A-3 528 954. This nonaqueous process is not preferred, however, because it is believed that it also generates relatively small amounts of high-molecular-weight products due to the gel effect arising in this "suspension polymerization". It is more likely that the gel effect gives rise to weak bonds in the main chain (HFP diads). A gel effect is most unlikely to occur in the aqueous emulsion
20 polymerization because chain propagation and chain termination take place on the surface of the latex particles.

The dispersion obtained from the polymerization is mechanically coagulated using a homogenizer (see EP-B-591 888) and agglomerated using a water-immiscible organic
25 liquid, such as gasoline, a technique well known in the art (see "Modern Fluoropolymers", editor John Scheirs, Wiley & Sons, 1997, page 227). The agglomerates are free-flowing beads with a diameter of from 0.5 to 2 mm. The free flowability is preferred for technical reliability in carrying out the subsequent work-up steps. The agglomerate is dried by flushing with nitrogen and then under moderate vacuum at temperatures up to 180°C.

30

Chemical coagulation of the agglomerate may also be employed. However, this is generally done using acids. This is not preferred, since it results in very high levels of

metal contaminants at all subsequent work-up steps. The agglomerate may then be fluorinated at temperatures of from 60 to 150°C, preferably at from 100 to 140°C with a mixture of fluorine in nitrogen. The mixture generally comprises 10% by weight of fluorine. Fluorination continues until at least 90 to 95% of the end groups of the original agglomerate have been eliminated. Higher fluorination temperatures can lead to a change in the MFI value which can be up to 30% and is difficult to control. This can lead to broadening of molecular weight distribution and adversely affect performance. The result is lack of reproducibility with an adverse effect on the quality and consistency of wires and cables coated with the polymer. Reaction times were not substantially shortened by higher temperatures, and higher fluorinating temperatures are therefore not considered to be advantageous. Moreover higher temperatures can lead to presintering or even sintering of the agglomerate, and sticking of the material to the walls of the equipment. The fluorination is carried out in a tumble drier which keeps the material in motion. This gives more homogeneous reaction conditions. The free-flowable agglomerate has to be as free as possible of fines and mechanically sufficiently stable enough for no substantial production of fines during post-treatment. Fines may impair the reliability of operation of the process. The agglomerate does not require the hardening which is disclosed in EP-B-222 945.

The fluorination of the agglomerate has two advantages. It is not diffusion-controlled, since the end groups reside on the surface of the latex particles. Reaction times are therefore relatively short. The unhardened agglomerate is sufficiently soft not to abrade metal contaminants from the wall of the tumble drier. Thus the level of metal contaminants is reduced. Neither feature holds for the fluorination of melt pellets. In this case the fluorination process requires higher temperatures and much longer reaction times to allow for diffusion control of the reaction. Furthermore, the hard, sharp melt pellets abrade a considerable amount of metal from the wall of the tumble drier. Increasing the reaction time results in higher levels of metal contamination. This contamination is difficult to remove. The level of metal contamination increased by up to two orders of magnitude when the pellet process was used.

The fluorinated agglomerate is subsequently melt pelletized.

Some comminution of the agglomerate takes place during drying and fluorination. This produces fines, which inhibit free flow of the material. It is advantageous to compact the fluorinated agglomerate before melt pelletizing. This gives a more reliable constant feed rate.

5

Melt pelletizing of fluorinated agglomerates provides many advantages over melt pelletizing of nonfluorinated agglomerates. Melt pelletizing proceeds practically without decomposition. The MFI value remains almost unchanged. This finding suggests that there is no substantial presence of weak linkages in the main chain. Corrosion of the equipment used is substantially reduced. The amount of metal contamination picked up is therefore insignificant. The emission of gaseous decomposition products at the die orifice is significantly reduced (e.g. by four orders of magnitudes). Thus the whole process becomes substantially more reliable. Die deposits are substantially reduced. Thus the process needs less attention. The melt pellets do not exhibit any discoloration, in contrast to melt pellets originating from non-fluorinated agglomerates, which are typically coffee brown in color when they leave the extruder.

10
15

The MFI value of the melt pellets produced via the process described above is only slightly increased by about 10%, compared to the MFI value of the copolymer from polymerization. It is therefore easier to achieve uniform quality.

20

As described in DE-A-195 47 909, the melt pellets are subsequently subjected to an aqueous treatment to remove volatiles and COF groups. Here too, the near absence of gaseous decomposition products and acidic end groups considerably reduces corrosion of the stainless steel water-treatment vessel. There is a reduction in further heavy metal contamination. Furthermore, water soluble salts originating from the production process are removed. The amount of extractable fluoride is reduced to less than 1 ppm.

25

Test Methods

The MFI value is measured according to ASTM D 1238 (DIN 53735) at 372°C with a load of 5 kg. The MFI value can be converted to the melt viscosity value in 0.1 Pas (Poise) by dividing 53150 by the MFI value (g/min).

30

The HFP content is measured via FTIR spectroscopy as disclosed in US-A-4 552 925. The absorbances at wave numbers 980 cm^{-1} and 2350 cm^{-1} , respectively, are measured on a film of 0.05 ± 0.01 mm thickness, produced at 350°C , with a FTIR-Nicolet Magna 560 FTIR spectrometer. The HFP content is calculated according to the following equation:

$$\text{HFP content (\% by weight)} = A_{980}/A_{2350} \times 3.2.$$

The end groups ($-\text{COOH}$, $-\text{COF}$, $-\text{CONH}_2$) are determined via FTIR spectroscopy as disclosed in EP-B-226 668 and US-A-3 085 083. A film of thickness 0.1 mm produced at 350°C is used together with a reference film of a material containing none of the end groups to be analyzed. A Nicolet Magna 560 FTIR spectrometer was used, with software in interactive subtraction mode. When the number of end groups is stated, this is the sum of isolated and associated COOH , CONH_2 and COF groups.

Melting points of the copolymers were determined by DSC by the method of ASTM D 4591-87 at a heating rate of 10 K/min . The melting point stated here is the peak temperature of the endotherm during the second melting process.

The breadth of the molecular weight distribution, characterized by the M_w/M_n ratio, was measured via rheological spectroscopy with an Advanced Rheometer Expansion System (ARES) supplied by Rheometric Scientific. Measurements were carried out at 372°C and evaluated by the method of W. H. Tuminello, Polym. Eng. Sci., 26, 1339 (1989).

Metal contents were measured by extracting the samples with 3% strength HNO_3 for 72 hours at room temperature and subjecting the extracts to atomic absorption spectroscopy.

The extractable fluoride ion content of the melt pellets was measured by the method given in EP-B-220 910. However, extraction was carried out only with water.

Example 1

A 1500 l stainless steel reactor was charged with 1000 l of deionized water with 3 kg of the ammonium salt of perfluorooctanoic acid. Air was removed by evacuation and
5 flushing with nitrogen. The reactor was heated to 70°C and the temperature kept constant. 2 kg of 25% strength aqueous ammonia solution were added.

The reactor was pressurized with TFE and HFP to 17 bar total pressure, the partial
pressure of HFP being 12.5 bar. The polymerization was started within 10 min by adding
10 1600 g of ammonium persulfate in solution in 5 l of deionized water. The pressure was kept constant by feeding a gaseous mixture of TFE/HFP into the reactor. The TFE/HFP weight ratio was 0.14. After 6 hours the reaction was stopped by interrupting the monomer feed. The monomers were vented off. The reactor was cooled to room temperature and then the contents were discharged. The solids content of the polymer dispersion was 29%.
15 The dispersion was practically free of coagulum. The MFI value was 20 g/min. The HFP content of the copolymer was 13% by weight. The melting point was 255°C. The copolymer had 660 COOH end groups per 10^6 carbon atoms. Mw/Mn was measured as 1.7, while an Mw/Mn value of 1.6 was calculated from the polymerization rate/time curve.
20 The dispersion was coagulated using a homogenizer and agglomerated using gasoline. The agglomerate was washed three times with deionized water and dried for 6 hours at 180°C in a tumble drier, first by purging with nitrogen and then under vacuum.

The resulting agglomerate was divided into two parts. One part was then melt-pelletized,
25 water-washed and dried giving a coffee brown color. It was fluorinated and again water-treated to remove residual COF end groups, whereupon the discoloration disappeared. This sample is called A0. The material had 43 end groups per million carbon atoms. The other part of the agglomerate was first fluorinated, then melted pelletized, treated with water and dried. This sample is called A1 and had only 18 end groups per million carbon
30 atoms.

At each processing step the content of iron, nickel and chromium was measured using the extraction method. Table 1 shows the results together with the amount of end groups.

Table 1:

- 5 Metal contaminations for samples A0 and A1 after the various steps of work-up. The agglomerate had 660 end groups.

Sample A0: Fluorination of the Melt Pellets (Comparison)

Steps of work-up					
metal ions	agglomerate [ppb]	melt pellets [ppb]	water-treated [ppb]	Fluorinated melt pellets [ppb]	Final product: water-washed melt pellets ^{*)} [ppb]
Fe	10	247	198	892	550
Ni	> 10	41	22	56	21
Cr	> 10	38	19	71	27

^{*)} 43 end groups per million carbon atoms

10

Sample A1: Fluorination of the Agglomerate (Invention)

Steps of work-up				
metal ions	agglomerate [ppb]	fluorinated agglomerate [ppb]	Melt pellets [ppb]	Final product: water-washed melt pellets ^{*)} [ppb]
Fe	10	14	18	14
Ni	> 5	> 5	> 5	> 5
Cr	> 5	> 5	> 5	> 5

^{*)} 18 end groups per million carbon atoms

The fluorination was carried out in a 300 l stainless steel tumble drier using a mixture of 10% fluorine in nitrogen, at 140°C (sample A0) and at from 100 to 140°C (sample A1).

- 15 Details are listed in Table 2. The fluorine mixture had to be replaced several times (replenishment). At the end of the fluorination, excess fluorine was removed by flushing air through the reactor. The excess fluorine was adsorbed by passing the air stream

through a bed of Al_2O_3 granules and through a scrubber comprising an aqueous slurry of CaCO_3 .

Table 2:

5 Fluorination Conditions for Samples A0 and A1.

sample	material form	reaction temp. °C	Number ^{*)} of replenishments	overall reaction time [h]	Final ^{**)} number of end groups
A0	Melt pellets	200	16	8.5	43
A1	Agglomerate	140	7	4	12

^{*)} replenishment every half hour, except for the last hour

^{**)} end groups are the total of COOH , COF and CONH_2 per million carbon atoms

10 Water treatment of the melt pellets (see DE-A-195 47 909) was carried out in a 1000 l stainless steel reactor. 200 kg of melt pellets and 400 l of deionized water with 1 l of 25% ammonia solution were charged to the reactor. The reactor was heated to 100°C and kept at this temperature for 4 hours for the nonfluorinated melt pellets and for 1 hour for the fluorinated melt pellets. This reaction time is required to bring the content of COF end groups to below 5 ppm. The reactor was cooled by replacing the water twice. The product
15 was dried by injecting hot air into the reactor. The melt pellets had an extractable fluoride ion content of 0.1 ppm.

Example 2

20 Sample A11 was run through a wire coating extruder under two different sets of conditions together with a commercial product designated C1. The production of sample A11 resembled that of A1, but the product had an MFI value of 24 g/min. Polymerization and work-up of A11 and A1 were identical. A11 has 28 end groups and an iron content of 18 ppb. The Mw/Mn ratio was 1.6. The calculated value was 1.7. The extractable fluoride
25 ion content was 0.2 ppm.

The coating conditions are listed in Table 3.

Table 3

Coating performance of the material according to the invention in comparison with a commercial product C1 and with sample A0

Run No.	1	2	3
Sample	A11	A11	C1
MFI g/min	24	24	21
Copper wire temp. [°C]	176 (350 F)	193 (380 F)	177 (350 F)
Cone length [cm]	5.1 (2.0 inches)	3.8 (1.5 inches)	5.1 (2.0 inches)
Die temperature [°C]	380 (716 F)	391 (735 F)	380 (716 F)
Extruder speed [rpm]	21.3	24.7	18.5
Line speed [m/min]	521 (1710 f/min)	611 (2006 f/min)	427 (1402 f/min)

5

The temperature profiles, not given in the table, were slightly adjusted to maximize the line output while maintaining the insulation eccentricity deviation between 0.00076 and 0.0018 cm (0.0003 and 0.0007 inches).

10

In runs 1 and 2 there were no marked die deposits and no cone fractures during the run time. In run 3 there was a considerable level of die deposits and cone fracture during an identical run time. When C1 was aged above its melting point (i.e., 250°C), it showed noticeable brownish discoloration.

15

Example 3

Samples A11, A12 and commercial products were run through a slightly different wire-coating extruder.

The coating conditions are listed in Tab. 4.

20

Table 4

Coating performance of the material according to the invention in comparison to two commercial products

Run No.	1	2
Sample	A11/A12	C2
MFI g/min	24/23	25
Copper wire temp. [°C]	193/190 (380 F/375 F)	177 (350 F)
Cone length [cm]	5.1 (2.0 inches)	5.1 (2.0 inches)
Die temp. [°C]	404 (760 F)	404 (760 F)
Extruder speed [rpm]	42.5	32.0
Line speed [m/min]	518 (1700 f/min)	415/417 (1390 f/min)

- 5 The temperature profiles were slightly adjusted to maximize the line output while maintaining the insulation eccentricity deviation between 0.00076 and 0.0018 cm (0.0003 and 0.0007 inches).

- 10 Run No. 1 did not show any noticeable die deposits, and only two cone fractures, during a period of 29 hours of extruding wires which were blue, green, orange, brown and white in color.

Run No. 2 showed a considerable level of die deposits and averaged 6 to 8 cone fractures during a run time of 24 hours.

Claims

1. A melt-processable, melt-pelletized copolymer which essentially comprises monomer units of
5 from 78 to 95% by weight of tetrafluoroethylene, from 5 to 22% by weight of hexafluoropropene and at most 3 mol% of fluorinated monomers copolymerizable with a mixture of tetrafluoroethylene and hexafluoropropene, and which has a ratio of weight average to number average molecular weight of less than 2, and has less than 80 unstable end groups per $1 \cdot 10^6$ carbon atoms, and is obtained by aqueous
10 emulsion polymerization.
2. A copolymer as claimed in claim 1 which comprises less than 200 ppb of heavy metals.
- 15 3. A copolymer as claimed in claim 1 or 2 which contains less than 40 unstable end groups per $1 \cdot 10^6$ carbon atoms.
4. A copolymer as claimed in claim 1 or 2 containing essentially no extractable fluoride.
20
5. A process for producing a copolymer which essentially comprises units of from 78 to 95% by weight of tetrafluoroethylene, from 5 to 22% by weight of hexafluoropropene and at most 3 mol% of fluorinated monomers copolymerizable with a mixture of tetrafluoroethylene and hexafluoropropene, and which has a ratio
25 of weight average to number average molecular weight of less than 2, and has less than 80 unstable end groups per $1 \cdot 10^6$ carbon atoms, by polymerizing the monomers by aqueous emulsion polymerization in an aqueous medium, coagulating the copolymer essentially by mechanical means, agglomerating the coagulated copolymer by bringing it into contact with an organic liquid which is
30 essentially immiscible with water, isolating the agglomerate, drying the agglomerate, without partial sintering, to give a free-flowing product, bringing the free-flowing agglomerate into contact with an effective amount of fluorine at a temperature of from 60°C to the presintering temperature for a time sufficient to essentially convert unstable end groups into stable end groups, melt-pelletizing the
35 fluorinated agglomerate, and bringing the melt pellets into contact with water at a temperature of from 60 to 130°C.

6. The process as claimed in claim 5, in which the aqueous polymerization medium used is essentially free from chain-transfer agents.
- 5 7. The process as claimed in claim 5, in which the polymerization medium used is water.
8. The process as claimed in claim 5, in which the polymerization medium used is essentially free from alkali metal ions.
- 10 9. The process as claimed in claim 5, in which, in the agglomeration step, the organic liquid used is free from halogen atoms.
10. The process as claimed in claim 5, in which the fluorination temperature is from 60 to 150°C.
- 15 11. The process as claimed in claim 5, in which the melt pellets are brought into contact with water comprising 0.01 to 1% by weight of ammonia or of a compound which liberates ammonia under the conditions under which the materials are brought into contact.
- 20 12. A process for reducing the frequency of cone fracture during the extrusion coating of wires, encompassing the steps of:
 - a) preparing a copolymer obtained from 78 to 95% by weight of tetrafluoroethylene, from 5 to 22% by weight of hexafluoropropene and at most 3 mol% of fluorinated monomers copolymerizable with a mixture of tetrafluoroethylene and hexafluoropropene, the ratio of weight average to number average molecular weight being less than 2;
 - 25 b) preparing a wire or conductive cable;
 - c) extruding the copolymer around the conductor at a temperature sufficient to provide uniform flow of the polymer.
- 30 13. The process as claimed in claim 12, where the polymer has less than 80 unstable end groups per $1 \cdot 10^6$ carbon atoms.
- 35 14. The process as claimed in claim 12 or 13, where the polymer comprises less than 200 ppb of heavy metals.

15. A coated wire produced by a process as claimed in any of claims 12 to 14.

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AbstractTetrafluoroethylene/Hexafluoropropylene Copolymers
with Higher Drawability

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A melt-processable, melt-pelletized FEP copolymer which essentially comprises monomer units of from 78 to 95% by weight of tetrafluoroethylene, from 5 to 22% by weight of hexafluoropropene at most 3 mol% of fluorinated monomers copolymerizable with a mixture of tetrafluoroethylene and hexafluoropropene, and which has a molar ratio of weight average to number average of less than 2 and has less than 80 unstable end groups per $1 \cdot 10^6$ carbon atoms, and is obtained by aqueous emulsion polymerization. After polymerization, the copolymer is coagulated, the coagulated copolymer is agglomerated, the agglomerate is isolated, dried avoiding partial sintering to give a free flowing product, the product is brought into contact with an effective amount of fluorine at from 60°C to the presintering, unstable end groups being converted into stable end groups. The melt pellets are advantageously treated in water with ammonia or a compound which liberates ammonia. The product is suitable for coating wires and cables.